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Self-Decontaminating Materials

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Surfaces that resist contamination through some combination of exclusion or reactivity may be grouped as Self - Decontaminating Materials (SDMs). A direct means to effect exclusion is to incorporate fluorine substituents into the surface of the SDM. Reactivity derives from the presence of chemically active groups, either at the surface or distributed throughout the medium. Whereas exclusion and catalytic reactivity tend to persist in the SDM after they have achieved their protective function, chemically active groups that combine or react with the contaminant will be consumed and may eventually be exhausted after extreme exposure. Applications now addressed in military operations center around minimizing penetration by chemical and biological agents until first responders are able to execute decontamination procedures or spontaneous decomposition occurs. However, filters, protective skin creams, coatings, and a spectrum of fabric products are ready for evaluation, and long-term development projects include SDM replacements for current shelter and filter materials.

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SELF-DECONTAMINATING MATERIALS

Joseph D. Wander[1]

ABSTRACT

Surfaces that resist contamination through some combination of exclusion or reactivity may be grouped as Self-Decontaminating Materials (SDMs). A direct means to effect exclusion is to incorporate fluorine substituents into the surface of the SDM. Reactivity derives from the presence of chemically active groups, either at the surface or distributed throughout the medium. Whereas exclusion and catalytic reactivity tend to persist in the SDM after they have achieved their protective function, chemically active groups that combine or react with the contaminant will be consumed and may eventually be exhausted after extreme exposure. Applications now addressed in military operations center around minimizing penetration by chemical and biological agents until first responders are able to execute decontamination procedures or spontaneous decomposition occurs. However, filters, protective skin creams, coatings, and a spectrum of fabric products are ready for evaluation, and long-term development projects include SDM replacements for current shelter and filter materials.

Introduction

Survival of organisms in the competition of Nature has depended on the evolution of defensive and offensive devices, many of which are also employed in a range of engineering contexts—bony plates and thickened skin textures correspond to armor, neurotoxic venoms are natural nerve agents, and the gland-and-fang system that introduces the venom is equivalent to hypodermic syringes and needles. Two other highly effective biological mechanisms afford self-protection to higher organisms: secretion and expectoration of mucus from respiratory tissue, which excludes inspired particles by collecting and removing them, and humoral immunity, whereby B-lymphocytes mount a chemical attack against foreign matter (antigens). A military engineering embodiment of these two mechanisms is Self-Decontaminating Materials (SDMs), substances or objects designed and fabricated to be able to exclude or actively deactivate pathogenic microorganisms or chemical warfare agents (CWAs).

Although the analogy between natural adaptation and military engineering is inexact, elements of it are instructive. The capacity to self-decontaminate comes at some cost to material

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properties and to other functions. To be useful, the new capacity must provide an advantage to the organism in the presence of the agent that induced development of the new capacity and, except in special circumstances, it may not significantly impair the performance of the organism in environments from which it is absent. In other words, incorporation of an SDM into an equipment item involves the same kinds of cost–benefit tradeoffs as any other engineering change to that system. And because the evolution of equipment designs within a generation of systems is much more gradual than changes between generations, we must expect that initial implementations will be incremental changes to existing materiel. Fundamental changes in design will follow the realization of benefits from these incremental changes.

General Considerations

CWAs and biological warfare agents (BWAs) span the range of physical and chemical states, from inorganic gases (chlorine, phosgene, HCN), through organic liquids (G-, H- and V- agents) and microbiological pathogens (*B. anthracis* spore, smallpox, ebola), to contaminated dusts. The actual risk of encountering CWAs and the likelihood and risk of encountering BWAs is still debated. Is it practical to aerosolize a microorganism that is normally transmitted by a vector and, if that can be accomplished, how effective will it be as a field weapon? This absence of consensus has limited progress toward the advancement of protective gear and shelters. Responding to a presumed attack by isolating combat personnel in a sealed and completely insulated environment affords immediate protection from the agent(s)---provided the containment survives any blast or other collateral effects associated with the mechanism (presumably airborne) of delivery of the agent(s). It also sacrifices the operational capability of surviving personnel, ensures extreme stress to both physiology and morale, aggravates the intimidation value of C/BWAs, and effectively concedes the purpose of the attack. At present, creating the perception of a C/BWA attack is very nearly as effective as actually making one. The mere image of a responder in less-confining protective gear would diminish the attractiveness of CWA to adversaries

Leaps forward in the state of protective technology will occur only following a thorough reassessment of actual risks of encountering a C/BWA and of the level of risk to personnel that one is prepared to accept in the event an attack occurs. Clearly the considerations for personnel assigned to special operations will be different from those for field medical or rear-area depot staff—and the likelihood of encountering toxic industrial materials will be much lower in a combat than in a civilian environment. Even from the perspective of developmental materials, the notion of a universal, "one-size-fits-all" protective technology is unrealistic and unattainable. It would be much more prudent to pursue development of a suite of technologies that offer graduated levels of protection against each of the threats considered significant, and to select a response appropriate to each situation as it is identified. Zero risk of casualties is a realistic design target for first responders to an industrial accident; it is thoroughly unrealistic in a combat situation.

Self-Decontaminating Materials

SDMs are appearing on the commercial landscape. A good example is self-cleaning

window glass, which is prepared by deposition of a series of very thin layers onto the silica surface. The lower layers include light filters and insulators, and the top layers contain titania (TiO_2) and tethered wetting agents. An impinging organic contaminant that is sufficiently polar to adhere to the hydrophilic top layer is gradually mineralized by a process in which sunlight activates the titania, which catalyzes oxidation of the contaminant by atmospheric oxygen. In the rain, impinging droplets spread across the entire surface, dissolving more-polar species (including salts and partially oxidized organics) and washing away dust particles. As long as the surface remains intact (the pane is not abraded, broken, or washed), the active materials in the various layers will continue to function. Several -ilities of this material are significant: affordability (reasonable), storability (long, nominally indefinite), supportability and maintainability (practically none), vulnerability (high), and observability (moderate to large).

A more-familiar commercial example is non-stick cookware. Transfer and distribution of heat are managed by selection and configuration of alloys in the utensil, and cooking residues are very loosely held by a coating of poly(tetrafluoroethylene) (PTFE) attached to the cooking surface. Like the multilayered glass, the pan is a multicomponent composite system in which the properties of individual materials act in concert, and in which only a certain order of placement of the layers is effective. The -ilities of the nonstick pan are similar to those of the glass, except that the coating is intrinsically less vulnerable but used in more-perilous circumstances.

Tenting materials are being modified to incorporate multiple functional coatings, including each of the three self-decontaminating mechanisms, at the surface. The significance of order of placement must be recognized, however, because PTFE is intensely hydrophobic and the wetting agent is strongly hydrophilic. A water droplet can be made to bead or to spread on a given surface, but not both. Only one material can go on top, so some properties will have to be selected to the exclusion of others. To make best use of the properties of the component materials, the equipment item will have to be designed to meet a limited number of specific requirements. A one-size-fits-all approach will compromise the effectiveness of the components and of the resulting equipment item. The following will illustrate roles and time to realization for SDMs in the context of several categories of equipment.

Water Disinfection

Support to deployed forces includes all aspects of maintaining personnel. Failure to provide for morale, health and welfare also diminishes effectiveness, so for this discussion we will define *equipment* broadly. Polystyrene resins have been modified to contain active forms of chlorine or iodine, both of which are highly effective, fast-acting, broad-spectrum antibiotics that kill by a nonspecific mechanism. The nonspecificity of the deactivating mechanism is a highly beneficial property because no single genetic response by a susceptible organism will allow it to become resistant. Evolution of drug resistance is a problem plaguing medicine and the pharmaceutical industry as overprescribing and maintenance of large populations of immune-compromised patients chronically expose large populations of microorganisms to varying levels of antibiotics. The effectiveness of the active agents (which act by specific mechanisms) in antibacterial cleaning materials will likewise be limited by evolution of resistant organisms, which is promoted by chronic use around the home and office.

Resins containing active halogens can be fitted into systems as small as canteens or as large as potable water treatment systems. At any scale, viability can be decreased as much as desired by extending residence time of water in the resin bed. In addition to the original complement of salts and suspended organics, the sterilized effluent will contain chloride or iodide from the treatment. If desalination is applied, it will have to precede disinfection until an efficient, halogen-resistant process is developed. Activated carbon or another adsorber for organics may be necessary if such contaminants are present in quantity, as in a compromised oil field. With these technologies, a treatment system could be assembled from modular elements containing only the specific activity required.

Table 1. Rate of kill of *E. coli* on surface of nonwoven material modified by incorporation of chlorine-carrying heterocyclic substituents and subsequently activated with sodium hypochlorite.

Time (seconds)	Percent killed
5	90
15	99
30	99.99
120	100

Air Purification

The same halogenated resins can be incorporated into air filters as entrained dusts, by fusion of the dust to the fiber, or by functionalization of the fiber. Modification of HEPA filters is a practical idea, but for present-generation C/B protection systems, replacement of the prefilters with an antibacterial equivalent are able to eliminate the load of organisms encountered by the HEPA stage. Although both the chlorinated and the iodinated resins will also react with some or all of the CWAs, the chemistry is not yet understood and may or may not eventually prove to be both beneficial and practical to apply.

Even if activity against CWAs proves to be insignificant, next-generation air-treatment systems may decrease their pressure loss by employing these materials in lieu of HEPA media for infection control. Other materials, SDMs or otherwise, will be required to develop the new designs. Introduction of antibacterial filters also portends significant health benefits by decreasing personnel exposure to airborne pathogens, *e.g.*, from sneezes into aircraft ventilation systems or to indigenous anthrax in agricultural areas.

Architectural Coatings

Architectural coatings are typically curing resins—*e.g.*, acrylates, polyesters, polyureas, and polyurethanes—into which are blended additives to impart desirable properties. Liquid CWAs are generally excellent plasticizers and able to penetrate resins, but BWAs will generally remain at the point of impact. Thus introduced halogen atoms must reside at the surface to exert an antibiotic effect, which requires that they be introduced into the structure of the resin (because

added particles are coated), and titania would have to be applied as a (possibly) fragile surface treatment to be exposed at the surface without attacking it.

Nucleophiles or other agents that would neutralize liquid CWAs, however, function inside the coating to intercept penetrating molecules. A polyurethane coating has been prepared from a very highly branched polyol, in which alcohol residues that did not fit into the forming polymer matrix were converted into primary amine groups. The amine group is expended when it reacts with a CWA and, unless it was applied at enormous thickness, the capacity of the coating would be exhausted by a limiting-case-scenario dose of liquid agent. In a reasonably tight interior environment, *e.g.*, a command center, such a coating would be adequate under most reasonable scenarios to clear its surface and prevent later migration out of absorbed CWAs.

A practical, antibiotic, polyurethane coating is being evaluated in institutional bathrooms. The chlorine carrier is incorporated into a diol that enters the growing chain and, after the coat cures, is activated by wiping on a dilute solution of hypochlorite (bleach). In contrast with the nucleophiles, the chlorine carriers are rechargeable and will participate in a cleanup exercise during which bleach is applied. For facilities that routinely apply bleach solutions as topical disinfectants, this involves no change of routine and the carrier will be restored to full charge with each cleaning. However, for the interior of aircraft cargo areas, the use of chlorine may disqualify the coating because of concerns about inducing corrosion.

Resistance to penetration can also be incorporated by incorporation of fluorine substituents. This contributes nothing to the process of decontamination, but isolates impinging agents at the surface, where they will be susceptible to treatment. Fluorinated polyureas are commercial products, acrylic fluoroesters and fluorinated precursors to polyesters and polyurethanes are available, and other partially fluorinated polymer systems are topics of research. Because it bonds poorly to most surfaces, the fluorine substituents must concentrate at the surface of the topcoat. The amount and distribution of fluorine substituents needed to achieve a useful extent of exclusion is a matter for optimization, and it will influence both cost and compatibility with chlorine carriers.

Fabrics

Impermeability has been the strategy in fabric design and selection for decades. Limitations on available materials dictated trading operational capability and comfort for hermetic isolation. The evolution of SDMs, together with semiporous materials that selectively pass small molecules, including water, oxygen, and carbon dioxide, offers promise of next-generation designs that may be slightly less protective but that will preserve a much greater measure of operational capability and personal comfort and morale. The selection of materials will depend on the intended usage of each fabric.

Undergarments

Odor-resistant sweat socks are commercial products, but most rely on antibiotic agents that are susceptible to the evolution of resistance and may be expected eventually to lose

effectiveness. Attaching a chlorine carrier to the fibers of a fabric offers an attractive alternative, and wear tests of socks so prepared have shown effective suppression of skin organisms with no adverse reactions reported. Many of the adverse effects of limited hygiene during deployments can be ameliorated by introduction of this capability into undergarments, and tests are planned to evaluate the efficacy and possible adverse effects of chlorine so delivered into intimate areas.

A slightly longer-term candidate application is the wearing of a large-coverage undergarment incorporating a chlorine carrier and/or possibly an organic-encapsulated nucleophile or other CWA-reactive material as a back-up system for leaks into current- and next-generation chemical protective gear. A short-term version could be fielded as a broad sweatband to be worn under the areas where parts of the protective gear overlap, to mitigate the effect of leaks. This could function as an alternative or an augmentation to the topical barrier creams.

Protective Gear

Incorporation of SDMs inside the meeting edges of components of existing protective chemical gear, perhaps as an inserted element, might mitigate or suppress leakage in. Placement of the same capability on the suit exterior might lessen the extent of contamination present or facilitate the processes of decontamination during entry into a shelter. Next-generation designs may layer semiporous membranes with SDMs and structural fabrics, and may presuppose a protective undergarment.

Battle Dress Uniforms

The fabrics of BDUs are treated with nonreactive coatings. Incorporation of available chlorine carriers is a straightforward process that can be accomplished in the field using standard laundry equipment, but the treatment developed for socks degrades the fabric somewhat and may deplete the nonreactive coatings. Bleach used in the activation process may also affect the color of dyes. Once these questions are settled and fixes or compromises determined, BDUs can be transformed by adding a hood and gloves, either as separate items or as rollouts under the cuffs and collar, into passive protective gear that will allow personnel a grace period to escape to a shelter or from a light-to-moderate contamination zone. Addition of a CWA-reactive underlayer or liner, and slight changes in the sealing methods between garment sections and in the hood will generate a moderately protective suit that might be useful to special operations units.

Soft Shelters

Emphasis on improving isolation and decontamination capability in airlocks will limit material improvements to current-generation soft shelter fabrics—particularly to harden protective liners against blast damage—and SDMs on the surface of protective gear might lessen pressure on the seals and decontamination methods in the port. More-extensive changes are possible in next-generation designs. A plausible transitional course might involve insertion of functionalized, porous panels that incorporate SDMs into tent walls, which would supplement the forced ventilation system and help dissipate heat and respiratory products. Such a step would test the trade of a decreased ventilation requirement for completeness of isolation, likely without

altering the function of and conditions inside the airlock. The ultimate evolutionary soft shelter may be able to neutralize traces of agent carried or drifting in, and to float ceramic panels on elastomeric fabrics to withstand small amounts of shrapnel.

Summary

A wide spectrum of polymers that are used in construction of equipment items of all types, commercial or military-unique, can be modified to incorporate functional substituents. Capabilities that can be introduced now include attraction or repulsion of water or of organic chemicals, nucleophilic and hydrolytic reactions with liquid CWAs, and chemical or photochemical oxidation. Continuing R&D activity is expected to provide additional capabilities.

Only certain combinations of SDMs and other materials are possible, and the sequence of assembly is also a limitation to design—some materials, *e.g.*, nucleophiles and oxidizers, titania and organic polymers, are incompatible and must be compartmented to coexist; some, *e.g.*, photocatalysts and rechargeable halogen oxidizers, must be at the surface to function. Within these boundary conditions and those attaching to other materials to be combined to create new devices or enhance the properties of existing equipment items, there is a vast amount of conjuring space, which will continue to expand as new materials appear. The task at hand is to identify needs, incorporate SDMs as appropriate to best satisfy them, and field these new capabilities.